EFFECT OF THE TIME TAKEN ON THE PERFORMANCE OF FABRICATED GAS–SOLID FLUIDIZED BED COLUMN FOR THE SEPARATION OF RARE EARTH ELEMENTS

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ABSTRACT

A gas–solid fluidized bed separator used for the separation of rare earth elements (REEs) from printed circuit board was design and fabricated. In this work, the effect of time taken on the performance of the fabricated gas-solid fluidized bed column for the separation of rare earth elements was study. Waste from electronic devices was grinded to powder forms with the particles sized less than 1.0 µm were used in this study. Beds column with different heights of sampling port were analyzed at 10 cm, 20 cm, and 30 cm while the air pressure was 15 psi, 20 psi and 25 psi were tried in this investigation. The rare earth elements were subsequently analyzed by float–sink testing. The results showed the weight percent of the fine powder increases with increasing the time taken for collecting the sample. However, the separation density decreased with increasing the sampling port height of the column.

Key words: Gas- solid fluidized bed column, Rare Earth Elements (REEs), Printed Circuit Board (PCB), Separation, Recycle.

ABSTRAK

Pemisah fluidized gas- pepejal digunakan untuk pemisahan unsur-unsur nadir bumi (nadir) dari papan litar bercetak adalah reka bentuk dan dibina. Dalam karya ini , kesan masa yang diambil terhadap prestasi ruangan katil direka gas- pepejal fluidized untuk pemisahan unsur-unsur nadir bumi adalah kajian . Sisa dari peranti elektronik telah dikisar kepada bentuk serbuk dengan zarah bersaiz kurang daripada 1.0 μm telah digunakan dalam kajian ini. Katil tiang dengan ketinggian yang berbeza pelabuhan pensampelan telah dianalisis pada 10 cm, 20 cm, dan 30 cm manakala tekanan udara adalah 15 psi, 20 dan 25 psi psi orang dibicarakan dalam penyiasatan ini. Elemen-elemen nadir bumi kemudiannya dianalisis dengan ujian apungan - tenggelam. Hasil kajian menunjukkan peratus berat serbuk bertambah baik dengan meningkatkan masa yang diambil untuk mengumpul sampel. Walaubagaimanapun , ketumpatan pemisahan menurun dengan peningkatan ketinggian pelabuhan pensampelan tiang.

Kata kunci: Gas pepejal ruangan cecair, Elemen-elemen bumi(nadir bumi), Litar Bercetak Lembaga (PCB), Perpisahan, Kitar semula

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LIST OF ABBREVIATIONS

Ce	*Cerium*
°C	*Degree Celsius*
Dy	*Dysprosium*
e.g.	*exempli gratia = for example*
Er	*Erbium*
etc	*et cetera*
Eu	*Europium*
Gd	*Gadolinium*
HCl	*Hydrochloric acid*
HREE	*Heavy Rare Earth Element*
HTS	*High temperature superconductor*
Ho	*Holmium*
ICP-MS	*The Interdisciplinary Center for Plasma Mass Spectrometry*
K	*Potassium*
kW	*Kilowatt*
La	*Lanthanum*
LAP	*Lanthanum phosphate*
LCD	*Liquid crystal display*
LED	*Light Emitting Diode*
LREE	*Light Rare Earth Element*
Lu	*Lutetium*
Mg	*Milligram*
m	*Meter*
Nd	*Neodymium*
NH_3	*Ammonia*
Ni	*Nickel*
Pr	*Praseodymium*
Pm	*Promethium*
R&D	*Research and development*
Ra	*Radium*

REE	*Rare earth element*
Sc	*Scandium*
Sm	*Samatium*
Tb	*Terbium*
Tm	*Thulium*
U_3O_8	*Uranium (V, VI) oxide*
TV	*Television*
U	*Uranium*
WEEE	*Waste Electrical and Electronic Equipment*
Y	*Yttrium*
Yb	*Ytterbium*

1 INTRODUCTION

Rare earth elements (REEs) are the 17 elements in the periodic table, 15 surrounded by the chemical group called lanthanides including yttrium and scandium. The lanthanides consist of the following elements: lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium as shown in Table 1.1. Rare earths are abounding in the earth's crust and some even more lavish than copper, lead, gold, platinum, and many other minerals. However, REEs are not concentrated enough to make them easily exploitable economically (Xiaoyue *et al.*, 2011).

Humphries (2012) stated that the REEs are typically split into two sub-group, the sub group of light rare earth elements (LREEs)—lanthanum through europium (atomic numbers 57- 63) and the heavier rare earth elements (HREEs)—gadolinium through lutetium (atomic numbers 64-71). Yttrium is also classified as a heavy element.

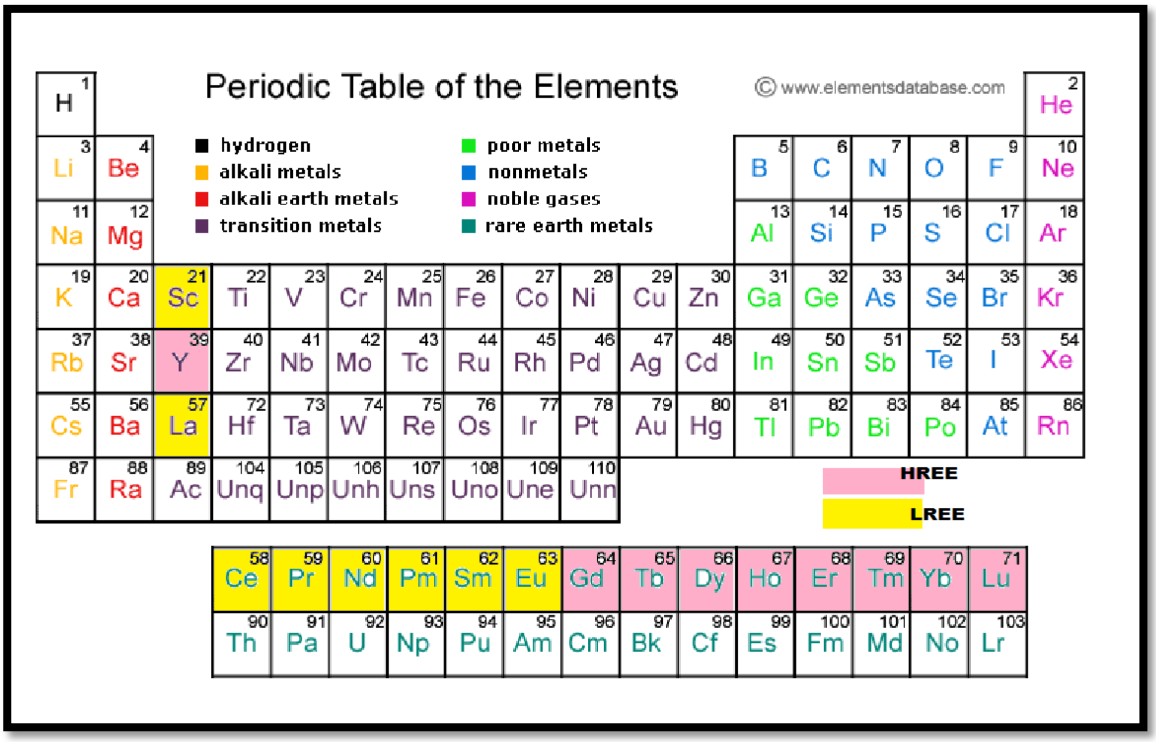

Figure 1.1: Periodic table of rare earth elements

1.1 Motivation and statement of problem

The raw material REEs is become more critical issues due to political tensions or shortages. In fact, REEs is really demanding for many important developing technologies regional industries. The rare earth group raw material as critical when after having carefully evaluated the political and economic situation of the producing countries, the level of supply concentration, the potential for substitution and the recycling rate is not enough. The situation it gives big impacts on the economy of each country due to the high dependency rate of REEs (Massari & Ruberti., 2012). Therefore, to defeat this issue, the recycle is the best ways because of the rapid development of electronic and information technologies has resulted in the arrival of low cost and enhanced the electronic products in the market resulting in the generation of the huge quantities of end-of-life electrical and electronic equipments (EOL-EEEs) due to their replacement (Lee *et al*., 2007).

Chen, (2011) highlighted that the most critical situation seems of rare earth groups to be due to the high import dependency rate, low substitution and low recycling rate. In fact, although their industrial demand is relatively small scale, they are noteworthy for many expanding high technology applications. Currently the global exploitation of rare earth elements has registered a steady and steeply increasing, but the supply of REEs has drastically diminished or decline.

The substitution for limited REE has shown that there are quite uncommon REE compounds by simple substitution of other compounds. In most cases replacements requires a completely new product design. The identified options for replacement in the case of major green applications are summarized below (Doris *et al*., 2011):

- Rare earth is currently used in approximately 14% of newly installed wind turbines with less gear design and technical advantages in terms of reliability. A shortage supply of rare earth will lead to a shift to alternative types of turbines. Further research on higher accuracy of traditional techniques with gear will support this substitution.

- Rare earth is commonly used in hybrid electric vehicles and also electric vehicles. Substitutions based on other electric motor design are predominantly available. However, R & D is needed for higher achievement of different types of existing electric motors and for the awareness of new motor concepts.
- Majority the new energy efficient lighting is containing rare earth element (compact fluorescent lamps, LED, plasma displays, LCD displays).The substitution is limited, especially for compact fluorescent lamps. R & D is required for alternative phosphors with high efficiency and high quality of light.
- Automotive catalysts contain cerium while catalyst for petroleum cracking and other industrial processes contain lanthanum. The replacements or substitution are really occasional, and R & D is needed for alternative catalysts.

REE distribute a lot of beneficial performance that can be irreplaceable by other material. They are becoming an important in the transition to a green and low-carbon economy. The increasing popularity of hybrid and electric cars, wind turbines and compact fluorescent lamps is causing an increase in the demand and price of REEs hence sparked the global competition for these resources (Binnemans *et al*., 2013). Recovery of rare earth element from liquid as well as solid waste is desirable due the lack or limited resources of rare earth elements. Instead of using pure raw material of rare earth elements we can recycle from the electronic waste.

Usually, REE can be found in electronic waste such as battery, chipboard, computer set, refrigerator and etc. Conventionally, this waste can be separated by using varies of method such as extraction, separation and purification. Therefore, it can illustrate the current situation of international markets, the availability of these strategic resources, the critical points of their supply, the possibility for substitution and recycling, and the environmental problems related to their extraction and the possible solutions to enhance their future supply security for the European countries.

1.2 Objectives

The aims of this work is to study the effect of the time taken on the performance of fabricated gas–solid fluidized bed column for the separation of rare earth elements.

1.3 Scope of this research

Separation of rare earth elements has been conducted by using fabricated fluidized bed column. The sample used is chipboard from electronic waste. The sample firstly grinded by physically crush using a crusher until it becomes to fine powder. The concentration of the powder is analyzed by using Sequential X-ray Fluorescence Spectrometer (Model No.XRF1700, Shimadzu, Japan) (XRF). Once the element concentration is known, the sample was injected into the fluidized bed column. The sample distributed according to their properties and density. This process separated the particles of sample which was collected at different sampling ports of the column. After collecting the sample at different sampling port, each sample will be analyzed for rare earth element concentration by using inductively coupled plasma-mass spectrometry. Consequently, a comprehensive kinetic study is on the effect of the time taken on the performance of fabricated gas–solid fluidized bed column for the separation of rare earth elements by varying the pressure of air flow rate and height of sampling port.

1.4 The recycling of rare earth elements

According to the research made by Doris *et al*., (2007) the recycling of rare earth elements could be stated as a very phenomenal issue until today. The recycling of rare earth metals has been undertaken most notably in Japan and there are number of extraction process but none of them has been developed commercially due to drawbacks on yield and cost. Principally, the recycling processes for the rare earth are quite complex and extensive if reuse is not possible and a physical and chemical treatment is necessary. Most of the recycling procedures are energy-intensive process. The recycling of rare earth from motors, hard disc and other electronic components which is the main post-consumer activities will require intensive dismantling.

Moreover, the potential shortages and the steep increase in price of rare earth are providing for the first time the opportunity to address the problem of today's rare earth supply in more depth and to seriously build up a recycling economy. The advantage of rare earth recycling includes the exploitation European resources, independence from foreign resources and also for environmental benefits also (Doris *et al*., 2011).

The recycling of rare earth has some advantages compared to the used of primary resource (Doris *et al*., 2011):

- The processing of secondary rare earth elements are free from radioactive impurities, the mining and further processing of primary rare earth is correspond with nuclear radiation coming from radioactive elements of natural deposits are commonly produces radioactive waste.
- The recycling requires some energy carriers and chemical but at the same time it saves significant amount of energy, chemical and emissions in primary processing chain. It is expected that most recycling will have a lot of benefit which is concerning air emissions, groundwater protection, acidification, eutrophication and climate protection.
- Dependence on foreign resources will be decreasing by supplying the European market with secondary rare earth materials.
- Europe is one of the globally large consumers of rare earths. Increasing amounts of waste from final products containing rare earths are arising in Europe.
- Apart from a few specialised industries and applications, the know-how in rare earth processing is quite low in Europe. The building up of know-how in recycling will widen the competency of enterprises and scientific institutions in Europe concerning rare earth processing.

1.5 Organisation of this thesis

This thesis will be divided into six chapters. First chapter is the introduction to the thesis and briefing about the project's idea such as the information about the rare earth elements and its advantages. It also included the application in various industries. There will also include problem statement, objectives and the scopes of the project.

Chapter 2 is for literature review which provides a description of the applications and general design feature in recycling of rare earth elements. A general review on the characteristics of the separation by using fluidized bed column processes for recycling rare earth elements. This chapter also provides a brief discussion of the advanced experimental techniques of recovery of rare earth elements. A summary of the previous experimental work on separation technique and its application also presented.

Chapter 3 gives a review of the fluidized bed column approach applied for the separation of the rare earth elements. This chapter is all about the method and procedures used in the experiment process. This chapter can be divided into five partitions which is design of fabricated fluidized bed column, The Interdisciplinary Centre for Plasma Mass Spectrometry (ICP-MS), sample preparation, parameter of study and the consumable procurements. The detail of the procedure was discussed in this chapter.

Chapter 4 is for the design of cylindrical fluidized bed column. The detailed explanation and characteristic is briefly described the fluidized bed column in this chapter. This will helps readers to understand the fluidized bed column thoroughly and completely.

Chapter 5 is for result and discussion of the data collection and analysis the results of the experiments. The collected data will be discussed and the results will be shown in the table. This will helps readers to understand the result thoroughly and completely. This chapter also included the discussion of the result that obtains from the experiments and factors that affecting the result.

Chapter 6 draws together conclusion and recommendation of this study. Hence, a summary of the thesis and outlines the future work which might be derived from the model developed in this work.

2 LITERATURE REVIEW

2.1 Overview

This research presents the experimental studies of gas-solid fluidized bed column which is dry separation technique in order to separate particles of rare earth elements. Research on recovery of rare earth elements is quite rare because the recycling processes for the rare earth elements are quite complex and extensive if reuse is not possible and physical and chemical treatment is necessary. However, potential supply shortage and the steep increase in price of rare earth are the opportunity to address problem of today’s rare earth supply in more depth and jump to seriously build up recycling economy.

2.2 Introduction

The concentration of rare earth elements (REEs) production in China raises the notable issue of supply vulnerability. REEs are used for many commercial applications including new energy technologies, electronic devices, automobiles, and national security applications. The examination of REEs for new energy technologies reveals a concentrated and complex global supply chain and numerous end-use applications. Therefore, placing the REE supply chain in the global context is unavoidable and becoming important resources (Humphries, 2012). In order to alter this issue, the rare earths elements can be recovered by recycle the waste from electrical and electronic equipment (WEEE).

The separation process of mineral particles using fluidization technique is described in this study. When a mixture of particles with sufficiently different physical properties is articulately fluidized, under some operating conditions the mixture separates and displays a behaviour called layer inversion (Rasul *et al*., 2000). This study supports: (1) a comprehensive criterion for particles of any type (size and density variant, only size variant or only density variant) to separate or mix and invert; and (2) mixing or separation regime map in terms of size ratio and density ratio of the particles for a given fluidizing. Therefore, knowing the physical properties of mineral particles, appropriate fluidization conditions can be chosen in order to separate them. Separations which use differences in specific gravity are one of the most commonly used, because of their effectiveness, low cost and operational simplicity. Recovery of rare earth material from electronic waste device provides multipurpose target which is control the hazardous materials, protect the environment against pollution, conserve the mineral resources and recover pure chemical compounds needed in the market. Moreover, the applied method is environmentally friendly with no hazardous by products and the cost of recovered products is competitive with the market price for the same chemicals prepared from primary resources.

2.3 Previous work on recovery of rare earth elements

The technology development of the last decades in the various sectors of the electronic industry has stimulated the replacement of obsolete gadgets. As a result, there is a growing disposal of obsolete computers and other electronic equipments into landfill sites throughout the world. To overcome this problem, the recovery of rare earth elements is one of the alternative ways.

According to the journal studied by Morais & Resende (2010) was studied recycle the rare earth elements from the tubes of colour TV set and computer monitor. Tubes of colour TV set and computer monitor present as coating, a powder containing a mixture of oxides and sulphides containing RE, mainly europium and yttrium. Despite the low amount recovered, the high commercial value europium makes it worthwhile. Therefore, study on the recycling of rare earth elements from the electronic waste device is valuable and desirable because it is currently incredibly commercial resource. The recovery of REE from electronic scraps and other metals is extremely important as the economic and environmental issues are concerned and also it leads to the recovery of other metals, e.g. lead, zinc, strontium, zirconium and indium, which are also present in computer monitor and TV screen coating powder.

Kumar V. *et al* (2013) was recommended to do research on physical separation process for eco-friendly recycling of rare and valuable metals from end-of-life DVD-PCBs because nowadays the end-of-life of printed circuit board was abundantly in any citizen. Even so, the PCBs made of from a lot of valuable elements and rare earth elements. Therefore, the PCBs is the most suitable component to recycle all the valuable elements. According to the journal from Kumar *et al.*, (2013), the separation of material is based on distribution of metallic and non-metal constituents in different size fractions. This study showed the enrichment of metals in coarser particles and non-metals in the finer particles by following pneumatic separation and froth flotation process. The result showed a grade of 88% with 75%recovery was achieved by froth flotation, but lower grade of 75% with 65% recovery were obtained by pneumatic separation with. Experimental results include metallic concentrate containing 91%, 82% and 95%metals in specific sizes such as -1500 + 1000 μm, -1000 + 850 μm and -850 + 500 μm size ranges correspondingly under optimized condition by pneumatic separation, while encouraging result in overall grade and recovery accomplished by froth flotation.

The liberation characteristic and physical separation of printed circuit board (PCB) was taken from the journal made by Wang *et al.*, (2011). The elaboration is highlighted of recycling of printed circuit board (PCB), beneficial because we can do both treatment of waste as well as recovery of valuable material. By using physical and mechanical method, a good liberation is the premise to further separation. In this study, two-step crushing process is in use, and standard sieve is applied to screen crushed material to different size fractions. Moreover, the liberation situation and particles shape in different size are observed. Then metal of the PCB is separated by physical methods, including pneumatic separation, electrostatic separation and magnetic separation.

2.4 Analysis methods of separation by using fluidized bed column

The fluidization technique has been widely used in industry. In the field of mineral separation industry, the fluidization technique is always used for the separation of minerals according to the difference of physical properties such as size, density and grade (Yanfeng *et al*., 2013). Fluidized beds is provide a method for particle separation based on density difference and are an established technology for particulate processing. The principles and techniques for effective particle separations by using the fluidized bed process is going to study and research in order to determine and investigate the behaviour of rare earth elements with suitable operating conditions

Rasul *et al*., (2000) highlighted that the mixture of particles with different nature characterized by size, density, shape and surface property is fluidize, a driving force for particle separation is established. This driving force depends on particle property differences and the operating conditions. Although material separation in mineral dressing represents a complex separation process, important insights can be obtained through experimental observations and theoretical analysis of mixing or segregation behaviour of binary mixtures in fluidized beds. A fluidized mixture of particles segregates and displays a behaviour called layer inversion under certain operational conditions.

Besides that, the present invention relates to methods and apparatus using fluidized bed principles for separating mixtures of solid particles of different densities, and more particularly to such methods and apparatus as are relevant to the grading of agricultural products or the separation of agricultural products from connected waste material (Albert *et al*., 1995). The use of density variation as a means of separating mixtures of particles is widespread. In agriculture, the separation and organization of produce on this basis is accomplished using both wet and dry methods (Albert *et al*., 1995).

According to Albert *et al* (1995) journal, the wet methods use a liquid as a medium with which to separate denser particles, which sink in the given liquid, from the lighter ones that will float at the top of fluidized bed column. Because of the use of fluids, however, these techniques have drawbacks which limit their application with agriculture products. Some liquids employed are expensive or present fire and social hazards when used in huge quantities. In addition, some agriculture commodities require pre-wetting in order to remove air bubbles and thereby permit their effective sorting in fluids. Other products are not suitable to processing in any liquid because the absorption of liquid usually affects the properties of the product. Finally, the liquids involved frequently become contaminated with foreign materials during the sorting process, affecting their density and requiring periodic changing or filtering.

Dry methods of sorting or cleaning of agriculture products are not impaired by the above described disadvantages. Some dry methods of sorting employ a form of compressed separation based on a combination of differing densities and differing aerodynamic properties associated with the components to be sorted. In such separation techniques, a gas, such as air, is forced upwardly through a moving bed of the mixture to be separated. This gas flow through the gaps of the particles of the mixture tends to disengage the particles from each other, permitting the gas flow to support at least some of the weight thereof. As a result, the bed of the mixture resembles a liquid of high viscosity, and the particles of the mixture are freed to a degree to migrate within the bed under the influence of physical forces that might tend to induce separation among the constituent components. However, Oshitani *et al* (2008) state in their paper that a wide range of apparent densities are possible by changing the air velocity for fluidization and by using a mixture of two types of particle with different densities for the fluidized medium.

Furthermore, according to the journal Kwant *et al* (1995), the separation occurs when a mixture to be separated is itself fluidized is not one that results exclusively due to differing density among the components of the mixture. Instead, the aerodynamic properties of the particles of the mixture also have a considerable impact upon the rate and quality of the separation that result (Kwant *et al*., 1995). The upward flow of gas through the mixture will tend to draw with it the less compact particles of the mixture, regardless of their density. Typically, the fluidization of such a mixture is effected as it passes down an inclined trough. At the discharge end of the trough the mixture of the materials has become somewhat stratified according to the combined density and aerodynamic property of the component particles. Nevertheless, such devices have several inherent drawbacks which render them less than optimally desirable in relation to the broad range of circumstances in which agriculture separators of the dry variety are nevertheless desirable (Kwant *et al*., 1995).

Piumsomboon *et al* (2013) pointed out that the fluidization regime also plays an important role in particle mixing process which is the vigorous particle movement yields a better mixed bed. In the case of binary, it may be impossible point to the fluidization regime for the entire bed. Each particle type may be fluidized according to a different regime. For binary fluidized system with a strong segregation tendency, it is reported that complete solids mixing is quite difficult to achieve. One can also imagine that at a moderately high gas velocity the flotsam particles are subject to conditions normally encountered with turbulent fluidization while the jetsam are fluidized in the bubbling regime (Piumsomboon *et al*., 2013).

2.5 Application of rare earth elements

Nowadays, there are demanding on the resources of rare earth elements due to the application by applying the rare earth element. The recycling is the best ways due to the rapid development of electronic and information technologies has resulted in the coming of low cost and enhanced the electronic products in the market increases the quantities of end-of-life electrical and electronic equipments (EOL-EEEs) due to their replacement (Lee *et al*., 2007).

Some of the major end uses for rare earth elements consist of use in automotive catalytic converters, fluid cracking catalysts in petroleum refining, phosphors in colours television and flat panel displays (cell phones, portable DVDs, and laptops), permanent magnets and rechargeable batteries for hybrid and electric vehicles, and generators for wind turbines, and various medical devices. There are important protection applications, such as jet fighter engines, missile guidance systems, antimissile defence, and space-based satellites and also communication systems.

Briefly, according to the journal studied by Ortegon *et al* (2010), rare earth element is the main material to create the wind turbines. Wind turbines are an important driver for the Nd-magnet demand. There are three different technologies for wind turbines and only one of them uses the Nd-magnets. All three systems are accessible on the market. These wind turbine work without gear, which makes them tough and a good candidate for off-shore applications. Furthermore, a new technology based on high temperature superconductor (HTS) rotors is under research and development.

The Figure 2.1 shows that the most applicable fields of application economically are magnets and phosphors. For phosphors, expensive REE such as europium and terbium are used. For magnets, mainly neodymium and praseodymium (medium price) and dysprosium and terbium (high prices) are used. The applications glass, polishing, ceramics and catalysts are relevant in terms of their volume but less relevant in terms of their value. The main reason for this is that the cheaper REE cerium and lanthanum are used very frequently for these applications Kingsnorth., (2010).

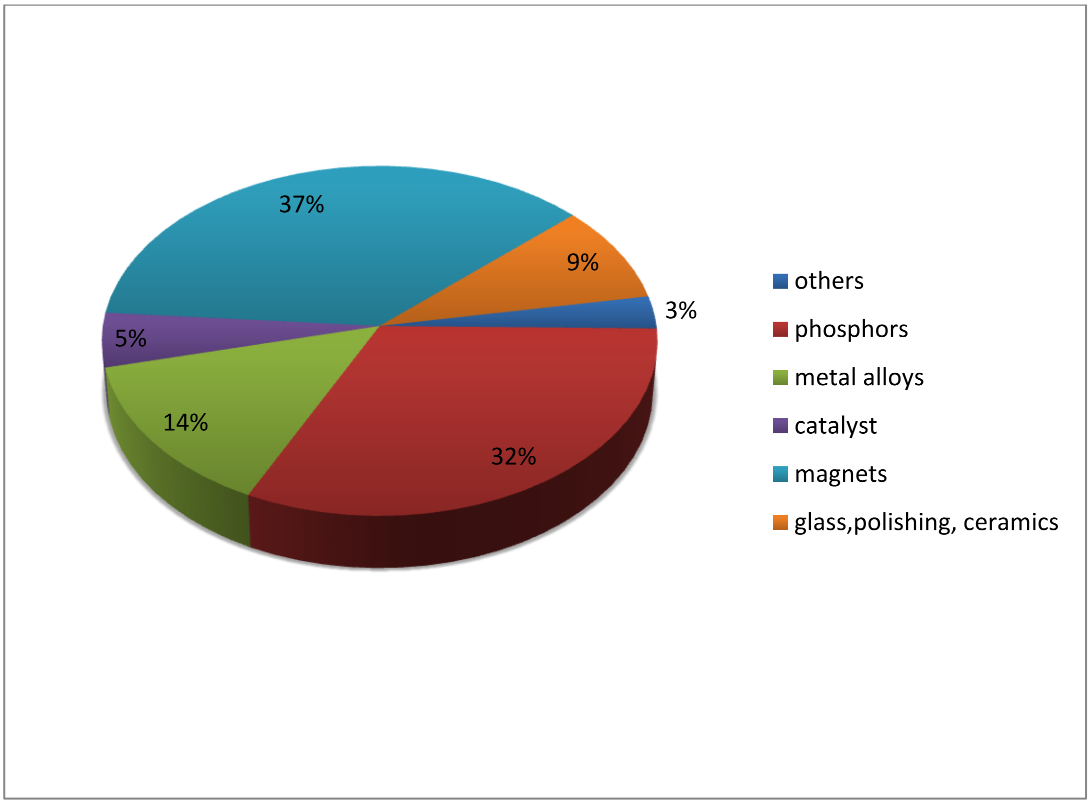

Figure 2.1: Global demand of rare earths in terms of economic value in 2008 according to Kingsnorth, (2010).

Furthermore, REEs have their own unique characteristics that are applicable and important in the production of worldwide industry. For example, erbium-doped super fluorescent fiber sources (SFSs) have been generally studied for the fiber-optic gyroscope (FOG) applications due to their high efficiency, broad bandwidth and low shot-noise limit (Lloyd *et al.*, 2010) and (Zatta *et al.*, 2002). Most of the studies as to